Synthesis, Characterization and Crystal Structure of 1,4,5,8-Tetrakis(Perfluoropyridin-4-yloxy) Naphthalene

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Abstract

1,4,5,8-tetrakis(perfluoropyridin-4-yloxy)naphthalene (tetra-PPN) was synthesized via a one-pot pseudo-five-component reaction of pentafluoropyridine and 5,8-dihydroxy-1,4-tetralindione under basic conditions in DMF. The asymmetric unit contains one half-molecule of tetra-PPN and data reveals that half of the molecule being related to the other via inversion symmetry. A detailed analysis of the intermolecular interactions of the compound has been performed using Hirshfeld surfaces. The optimized geometrical parameters and calculated spectroscopic features obtained by quantum chemical calculations using density functional (DFT) methods. In addition, to support the experimental results, the 19F NMR values are obtained using B3LYP method. The obtained results are compared with experimental values show a very good agreement with the experimental data.

Keywords: Pentafluoropyridine; Tetralindione; One-pot synthesis; Single crystal; X-ray structure; DFT

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Introduction

Organofluorine compounds find many different applications, ranging from pharmaceuticals and agrochemicals to advanced materials and polymers [1]. The unique properties of the fluorine atom, such as high electronegativity, low polarizability, and small covalent radius together with the great strength of the C-F bond and its tendency to increase lipophilicity of organic molecules are behind its wide impact. Circa 30–40% of agrochemicals and 20% of pharmaceuticals contain at least one fluorine atom [2,3].

Many perfluoroheteroaromatic compounds such as perfluoroquinoline [4] and pentafluoropyridine, in which all the hydrogen atoms of the heterocyclic rings have been replaced by fluorine atoms, have been investigated since the early 1960s [2,5,6]. The most important reaction of pentafluoropyridines involves the replacement of the para-fluorine atom by nucleophilic reagents allowing the synthesis of new organofluorine compounds such as heterocyclic and macrocyclic perfluoro systems [7-9]. Theoretical calculations were done using the density functional theory (DFT) with B3LYP methods using 6-31+G (d,p) basis set to support our spectroscopic and structural properties of the studied molecule. The geometric structural parameters and 19F NMR results were calculated and compared with the experimental results.

Results and Discussion

Previously we have described the synthesis of some 4-substituted tetrafluoropyridine systems from reaction of pentafluoropyridine with tetrazole-5-thiol, piperazine, hydroxylated naphtoquinones and antraquinones [10-12]. Here we describe the reaction of pentafluoropyridine with 5,8-dihydroxy-1,4-tetralindione, resulting in 1,4,5,8-tetrakis(perfluoropyridin-4-yloxy)naphthalene (tetra-PPN) **(Figure 1)**. Whilst many reactions of nucleophiles with pentafluoropyridine have been reported, processes involving one-pot pseudo five-component reactions of pentafluoropyridine with nucleophiles are uncommon.

When 5,8-dihydroxy-1,4-tetralindione was treated with pentafluoropyridine in the presence of potassium carbonate
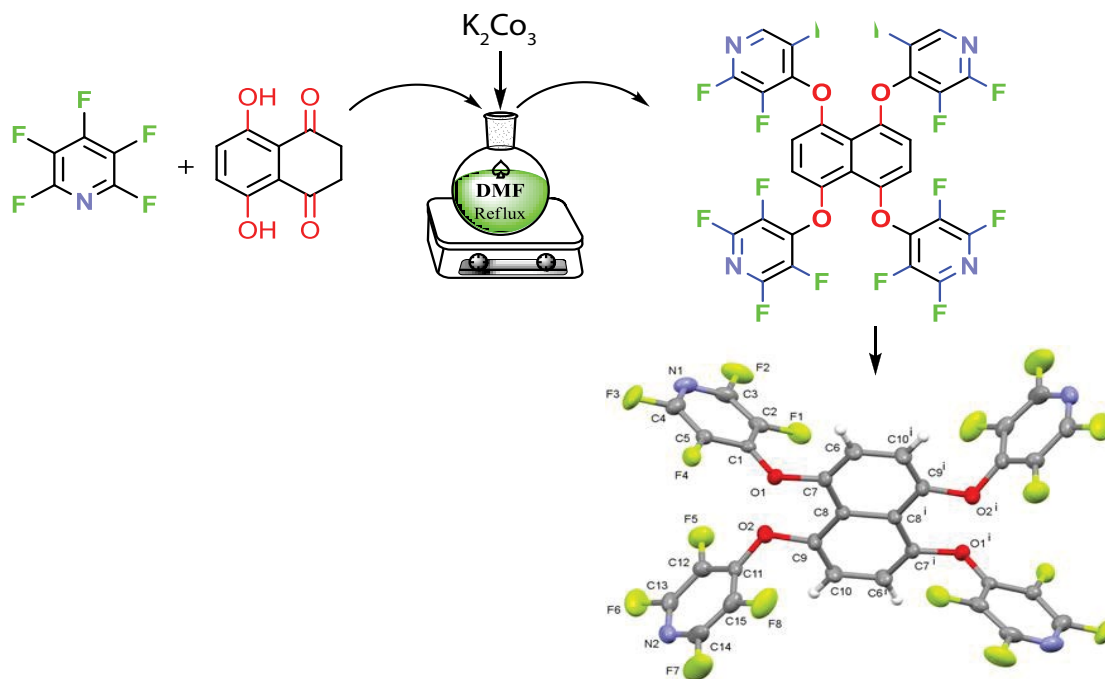
Figure 1   Synthesis of 1,4,5,8-tetrakis(perfluoropyridin-4-yloxy)naphthalene (tetra-PPN).
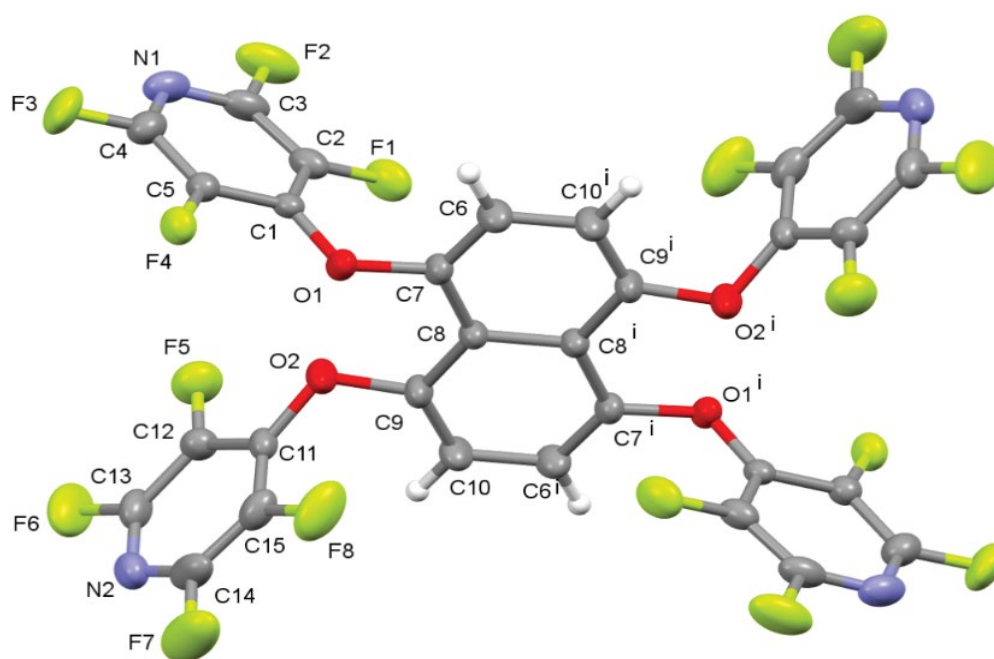
Figure 2   Molecular structure of 1,4,5,8-tetrakis(perfluoropyridin-4-yloxy)naphthalene (tetra-PPN) with displacement parameters at 40% probability level.

in DMF tetra-PPN was formed in moderate yield. The single-crystal X-ray structure of the structure (tetra-PFN) (1) is shown in **Figure 2.** Structure crystallizes in the monoclinic crystal system with space group P21/n which appears to be centrosymmetric, with one half of the molecule being related to the other via inversion symmetry. Further details of the structure determination are given in **Table 1.**

The average distance between neighbouring fluorine atoms is 2.90 Å length. An intermolecular quasi-hydrogen bond C10-H⋯N1 connects (Hydrogen-Acceptor distance=2.76(1) Å) the pyridine unit with the naphthalene. However, the second pyridine nitrogen N2 exhibits a σ-π interaction with a neighbour pyridine. The molecular packing is given in **Figure 3.**

The intermolecular interactions are illustrated by a Hirschfeld

Table 1 Crystallographic data for the structures provided.

Empirical formula	$C_{30}H_4F_{16}N_4O_4$
Formula weight	788.37
Temperature	292(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 2_1/n
Unit cell dimensions	a = 5.7900(2) Å
	b = 18.8129(8) Å
	c = 13.3418(5) Å
Volume	1435.19(10) Å^3
Z	2
Density (calculated)	1.824 Mg/m^3
Absorption coefficient	0.192 mm^{-1}
F(000)	776
Crystal size	0.50 x 0.10 x 0.07 mm^3
Theta range for data collection	2.17 to 28.26°.
Index ranges	-7<=h<=7, -24<=k<=24, -17<=l<=17
Reflections collected	6319
Independent reflections	3427 [R(int) = 0.0741]
Completeness to theta = 25.00°	99.0 %
Max. and min. transmission	0.9867 and 0.9100
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3427 / 0 / 245
Goodness-of-fit on F^2	0.974
Final R indices [I>2sigma(I)]	R1 = 0.0687, wR2 = 0.1717
R indices (all data)	R1 = 0.1856, wR2 = 0.2229
Extinction coefficient	0.018(5)
Largest diff. peak and hole	0.335 and -0.215 e.Å^{-3}

Table 2 Selected bond lengths (Å) and angles (°) with the selected torsion angles (°) for tetra-PPN. The calculated values are for gas phase.

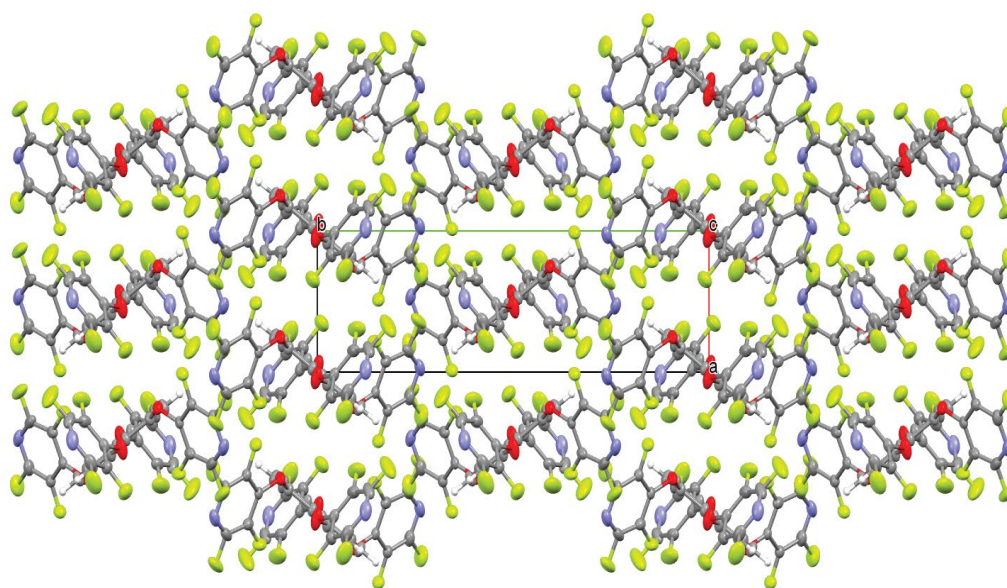|	Bond lengths			Bond angles	
	Exp.	Calc.		Exp.	Calc.
C9-O2	1.403(4)	1.397	C9-O2-C11	118.6(2)	121.9
O2-C11	1.348(4)	1.351	F8-C15-C11	117.6(2)	121.2
C15-F8	1.345(5)	1.345	F5-C11-C12	122.0(2)	119.8
C14-F7	1.331(6)	1.338	F6-C13-N2	115.2(2)	117.4
C13-F6	1.335(5)	1.337	N2-C14-F7	119.3(2)	117.5
C12-F5	1.322(4)	1.341	C7-O1-C1	120.0(3)	120.7
O1-C7	1.408(4)	1.392	O1-C1-C2	127.3(3)	124.2
C1-O1	1.354(4)	1.355	C1-C2-F1	121.2(4)	120.5
C2-F1	1.344(4)	1.342	C2-C3-F2	117.9(3)	118.5
C3-F2	1.347(5)	1.337	F2-C3-N1	116.0(3)	117.5
C4-F3	1.353(5)	1.337	N1-C4-F3	117.0(2)	117.5
C5-F4	1.342(4)	1.340	F3-C4-C3	118.3(2)	118.7
			C4-C5-F4	121.3(2)	121.4
		Dihedrals		
			C9-O2-C11-C15	60.7(2)	27.04
			C7-O1-C1-C5	-160.3(3)	-137.53

(calc. -173.94 ppm) and -162.54 ppm ppm (calc. -179.69 ppm). In Tetra-PPN, two chemical shift of ortho and meta position, there may be hindered rotation about the C-O bonds. The 1H NMR spectra of tetra-PFN shows the protons of the naphthyl ring at δ=7.25 ppm.
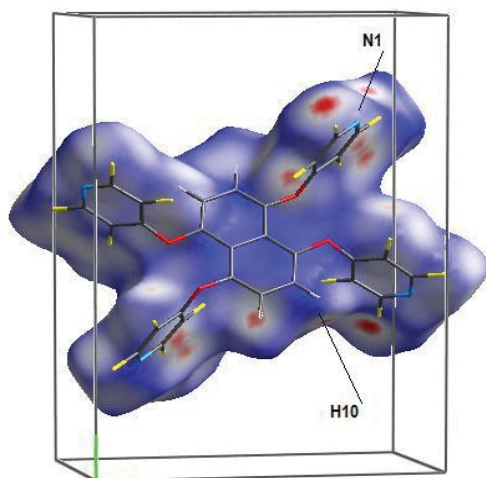
X-ray crystallography

The single-crystal X-ray crystallographic diffraction data were collected at 293 K with a Rigaku R-axis Rapid-S IP-detector diffractometer with graphite-monochromated Mo-$K\alpha$ radiation (λ=0.71073 Å). Suitable single crystal of tetra-PPN was mounted on the tip of a glass fiber with silicone grease and transferred to the diffractometer for data collection. The collection of frames of data, indexing of reflections, and determination of the lattice parameters and the integration of the intensity of the reflections were performed with the CrystalClear (Rigaku/MSC Inc., 2005) software [16]. All of the structures were solved by direct methods with SHELXS-97 [17,18] and refined with SHELXL-97 [19,20]. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were fixed at calculated positions and refined isotropically with a riding model. The final difference Fourier maps showed no peaks of chemical significance. The crystallographic data are summarized in **Table 2**. CCDC 1521820 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Computational methods

The calculations were performed using the Gaussian 09 package [21]. The geometries of the molecule has been fully optimized in the ground state at the B3LYP/6-31+G(d,p) computational level [22-24]. The vibrational frequencies were calculated at the same theoretical level to confirm that all optimized ground configurations had no imaginary frequencies and the ground-state minima were on potential energy surfaces. The 19F NMR chemical shifts were obtained using the Gauge-Including

surface [13-15], which is constructed from points with fixed ratio (usually 0.5) between the contribution to the electron density from a molecule and the contribution from electron density from the whole crystal. Particularly instructive is to colour-code the surface by the distance to the nearest atom within the surface or external to it. Short interatomic distances on both sides on the surface are plotted red, longer ones in blue **(Figure 4)**. Van der Waals interactions are marked red (N1, H10). No red marking on the surface was found in the vicinity of N2.

In the calculation, the initial geometry of the molecule was obtained from X-ray results and it was optimized using B3LYP method with B3LYP basis set. The optimized structure is given in **Figure 5.** The selected bond lengths, bond angles are given in **Table 2.** As seen in **Table 1,** and chart 1 and 2, the obtained values are in good agreement with the experimental values. The maximum deviation is 0.019 Å for C12-F4 bond length and 3.62o for F8-C15-C11 bond angle. In addition, the orientations of the tetrafluoronaphthalene rings on the planar naphthalene ring are 27.04o (C9-O2-C11-C15) and 47.53o (C7-O1-C1-C2).

NMR spectroscopic characterization

Tetra-PPN was characterized by ^{19}F NMR data. It is obtained that the experimantal and calculated values are compatible with each other. The fluorine atoms located in the ortho position relative to the ring nitrogen has a chemical shift of -87.61 ppm (calc. -106.66 ppm) and -91.69 ppm (calc. -110.16 ppm) and the fluorine resonance located in the meta position occur at -156.69 ppm

Figure 3 Crystal packing of tetra-PPN viewed down along the c-axis.

Figure 4 Hirshfeld surface of tetra-PPN.
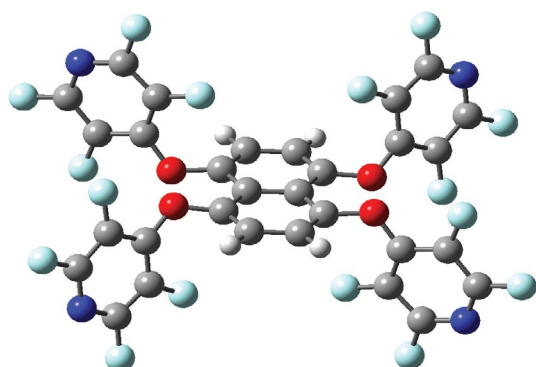
Figure 5 The optimization structure of 1,4,5,8-tetrakis(per-fluoropyridin-4-yloxy)naphthalene (tetra-PPN).

Atomic Orbital (GIAO) method [25,26] with B3LYP/6-311++G(d, p) method in CDCl3 solvent. The values of the chemical shifts were estimated using δCCl3F value for shielding constant of trichlorofluoromethane (CCl3F) florine obtained by the same approach, according to expression δcald.=δCCl3F-δ.

Conclusion

We have demonstrated that all four oxygen atoms in tetralindione can react with pentafluoropyridine to afford of 1,4,5,8-tetrakis(perfluoropyridin-4-yloxy)naphthalene, which was characterized spectroscopically and via single crystal X-ray diffraction, in a one-pot synthesis.

Experimental

General information

All materials and solvents, purchased from Merck and Aldrich, were used without any additional purification. The melting points of the products were determined in open capillary tubes using BAMSTEAB Electrothermal apparatus model 9002. The ^{1}H NMR spectra were recorded at 300 MHz and referenced to TMS. The ^{19}F-NMR spectra were recorded at 376 MHz. In the ^{19}F-NMR spectra, up field shifts were quoted as negative and referenced to CFCl3. Silica plates (Merck) were used for TLC analysis.

Preparation of 1,4,5,8-tetrakis(perfluoropyridin-4-yloxy)naphthalene (tetra-PPN)

Pentafluoropyridine (0.32 g, 2 mmol), 5,8-dihydroxy-1,4-tetralindione (0.1 g, 0.5 mmol) and potassium carbonate (0.5 g, 4.0 mmol) were stirred in DMF (5 mL) at reflux temperature for 6 h. The reaction mixture was evaporated to dryness and the solid product was then recrystallized from ethyl acetate and chloroform to give tetra-PPN (0.3 g, 45%) as red crystals; mp 380°C dec.

^{1}H NMR (CDCl3): δ (ppm) 7.25 (s, 4H, CH)

^{19}F NMR (CDCl3) δ (ppm) -87.61 (s, 4F, F-2,6), -91.69 (s, 4F, F-2',6'), -156.69 (s, 4F, F-3,5), -162.54 (m, 4F, F-3',5').

Conflict of Interest

None declared under financial, general, and institutional competing interests. I wish to disclose a competing interest(s) such as those defined above or others that may be perceived to influence the results and discussion reported in this paper.

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